Innovations in Cavity Enhanced Laser Absorption Spectroscopy: Using *in situ* Measurements to Probe the Mechanisms Driving Climate Change

Gregory S. Engel
Harvard University
12 Oxford Street
Cambridge, MA 02138

Elisabeth J. Moyer
Harvard University
12 Oxford Street
Cambridge, MA 02138

Frank N. Keutsch
Harvard University
12 Oxford Street
Cambridge, MA 02138

James G. Anderson
Harvard University
12 Oxford Street
Cambridge, MA 02138

***Abstract*— Probing the complex responses of the atmosphere and elucidating causal relations to anthropogenic forcings demands repeated *in situ* measurements capable of quantifying a host of atmospheric species, including isotopomers, radicals and tracer species. Over time, these measurements will serve both to validate measurements from the AURA satellite program and to probe the chemistry and physics of small scale phenomena that drive regional scale changes. Practically, such measurements present specific criteria for instrument design: the detection technique must be sufficiently general to allow many species to be monitored, sufficiently compact and lightweight to allow flights on small aircraft, sufficiently robust to withstand the rigors of flight, and sufficiently simple to produce reliable and trusted results. Advancements in Cavity Enhanced Laser Absorption Spectroscopy address all these concerns while offering exceptional sensitivity due to long effective pathlengths ($> 30\ km$) of the high-finesse optical cavity [1]. Historically, such sensitive measurements have been plagued by stability issues arising from limitations in light sources, mechanical design, detection electronics and data reduction techniques [2] [3]. We will demonstrate technological advancements in each of these areas to allow scalable, modular, lightweight instrument construction with the necessary sensitivity for the most demanding measurements while providing multiple, direct calibration methods. In particular, we will focus on advancements in Integrated Cavity Output Spectroscopy (ICOS) and Cavity Ringdown Spectroscopy (CRDS) improving detection limits to $2.9 \times 10^{-11} cm^{-1}/\sqrt{Hz}$ in a flightworthy configuration.**

I. Introduction

Addressing the couplings between climate change and atmospheric chemistry requires detailed analysis of both small-scale atmospheric phenomena as well as regional and global coverage of broader trends. These complementary measurements will provide both the detail and the context necessary to fully understand causal relations between local, regional and global changes. Probing the the chemistry and physics of the couplings between small-scale, isolable mechanisms and large scale changes will provide the basis for precise understanding of the evolution of the climate system. In addition, such complementary measurements are necessary for calibration and validation of all the instruments taking part in this effort.

A. Scientific Demands on in situ Atmospheric Measurements

Recent advancements in satellite measurements and scheduled improvements in the coming years demand immediate improvement in *in situ* measurement capabilities and in the infrastructure required to support the validation of the new instrumentation. The *in situ* measurement community must become more agile, responding quickly to the needs of the larger atmospheric community. Airborne measurements will need to shift from biannual missions to more frequent missions to provide data as the need arises. Widely temporally-spaced, isolated experiments fail to provide the necessary boundary conditions for efficient atmospheric modeling and fail to address the validation needs of the satellite community. Frequent missions, even those of smaller scale, will generate more useful data to determine convection and chemical events that lead to regional-scale phenomena. Additionally, more frequent missions will spur more rapid innovation of *in situ* measurement techniques by significantly reducing the time between opportunities for atmospheric trials.

B. Requirements for Evolving Instrument Technology

As the mission of the airborne measurement community evolves to include more collaboration with the satellite community and to address phenomena on a larger geographic and temporal scale than can be accommodated on any given single mission, the requirements for the instrumentation must evolve as well. Without loss of sensitivity, accuracy, or precision, instrument design must be sufficiently versatile to allow rapid deployment for any of a host of atmospheric species, with the facility to expand as the demand arises. Practically, this requirement can only be met by absorption spectroscopy. Other techniques, though extremely valuable will not adapt as easily to quantifying new species. The *in situ* community must preserve its heritage and continue to innovate on all available platforms, but future development of absorption platforms appear most promising for offering the agility and scalability future measurements will demand.

Beyond simply developing the capability to measure new species quickly, such measurements must be possible on an ever-leaner budget in order to provide scalability for frequent

measurements and for technological improvement. By incorporating technology developed by other industries, such as communications, defense and materials science, lower-cost instrumentation can be developed without sacrificing quality.

Similarly, by utilizing mature technology from other industries, we allow for significant simplification and miniaturization creating a situation that is advantageous both in simplicity of calibration and in reduction of size and of weight. The reduction in size and weight offers significant benefits by permitting the use of lower cost, smaller aircraft platforms for *in situ* measurement. The availability of these smaller airborne platforms directly impacts the feasibility of undertaking more frequent missions.

We will demonstrate the feasibility of simple, direct spectroscopic techniques utilizing spectroscopic technology developed for atmospheric science and leveraging technology in related industries to create *in situ* instrumentation based on absorption spectroscopy. The instruments provide sensitivities comparable to or better than those available today.

II. Cavity Enhanced Spectroscopic Techniques

Innovation in optical coating technology driven by communications and defense industries in the past decade has dramatically changed sensitivity thresholds for absorption spectroscopy. By using a high finesse ($F > 30000$) stable optical cavity consisting of two highly reflective mirrors ($R > 99.99\%$), highly sensitive absorption measurements can be made with modest sample volumes. Using such a cavity-enhanced system, a typical 1m sample cell length yields an effective pathlength of 10km. Leveraging this effective pathlength into a realizable spectroscopic gain is not a trivial task, but we will present three techniques designed to take advantage of these benefits.

A. Cavity Ringdown Spectroscopy

Cavity Ringdown Spectroscopy (CRDS) is the most mature of the cavity enhanced techniques [1] [4] [5]. In a CRDS system, the stable optical cavity is pumped using a pulsed laser source, yielding an initial intensity of I_0. The intensity, I, of the light inside the cavity then evolves according to the differential equation,

$$I(t) = I_0 \left(R \exp\left(-\alpha\left(\nu\right) L\right)\right)^{\frac{ct}{L}}, \tag{1}$$

where L is the length of the cavity, R is the reflectivity of the mirrors, $\alpha(\nu)$ is the wavelength dependent absorption cross-section and c is the speed of light. Thus, the intensity within the cavity evolves as

$$I \approx I_0 \exp\left(-\frac{t}{\tau}\right) \quad \text{where} \quad \tau = \frac{L}{c\left(1 - R + \alpha\left(\nu\right) L\right)}. \tag{2}$$

From this equation, we can see that the light in the cavity should decay as a single exponential with a characteristic time, τ. The time constant, τ, depends on the length of the cavity, the reflectivity of the mirrors, and the absorption within the cavity. By monitoring this decay constant, τ, in the presence and absence of an absorber, we can determine the absolute concentration dependent absorption coefficient directly. To first order, this process is independent of laser power (which is important with pulsed sources), and the sensitivity is limited only by our ability to determine the decay constant [6].

Though simple and direct, many experimental concerns make this technique rather difficult to implement. First, fitting nonlinear decay signals with sufficient accuracy in the presence of noise is a difficult task. Secondly, because the mirrors have finite extent, the light in the cavity is best represented by a superposition of transverse cavity modes, each with a slightly different characteristic decay constant due to the aperture effect at each pass through the cavity [7]. In addition, fluctuations in the cavity alignment in a passive cavity create additional changes in the decay constant.

Despite these challenges, in mode-matched systems (maximizing the contribution of the TEM_{00} mode) with an actively locked cavity, sensitivities on the order of $8.8 \times 10^{-12} cm^{-1}/\sqrt{Hz}$ have been achieved [8]. However, actively locked cavities of this type will not prove feasible for in flight use both because of complexity and because of the need for vibrational isolation. We will demonstrate that with a flightworthy passive cavity sensitivities of nearly the same level, $2.9 \times 10^{-11} cm^{-1}/\sqrt{Hz}$, are possible. With CRDS, the accuracy of the concentration dependent absorption cross-section can be tied directly to the timebase of the digitizer and to the length of the cell, while the precision is determined by the quality of the fitting algorithm and stability of the optical system. However, we recommend, nonetheless, that *in situ* instruments fly with a known calibration standard to produce the most trustable results possible.

B. Cavity Attenuated Phase Shift Spectroscopy

Cavity Attenuated Phase Shift (CAPS) Spectroscopy uses the phase delay introduced by the optical cavity as a monitor of the time constant [9]. In an optical analog to an electrical RC filter (which displays the same exponential response to a step function demonstrated above), an amplitude modulated signal with a sine wave envelope of frequency, f_{mod}, can be used to pump the optical cavity. Noting that the phase shift, ϕ, is given by

$$\phi = \tan^{-1}\left(\frac{-1}{2\pi f_{mod} tau}\right), \tag{3}$$

we can see that the phase shift is a direct measure of the decay constant, τ, for a known modulation frequency, f_{mod}. Because the derivative of the phase shift is maximized at the 3dB point of the cavity, the optimal frequency for modulation is given by

$$f_{mod} = \frac{1}{2\pi\tau} = \frac{c\left(1 - R + \alpha\left(\nu\right) L\right)}{2\pi L}. \tag{4}$$

CAPS spectroscopy has many advantages over CRDS including a higher duty cycle and higher signal strengths on the detector making the measurement much less susceptible to detector noise limitations. At the same time, the detection bandwidth can be extremely narrow further limiting contributions from detector and electronic noise and eliminating the

need for fast detection electronics. CAPS spectroscopy also makes use of continuous wave laser sources, which are much more readily available than pulsed sources in the vibrational region of the mid-infrared spectrum.

Despite providing a direct measure of the cavity decay constant, CAPS systems have been limited by the ability to determine the phase of a noisy signal from a passive cavity. The noise on the signal comes from the laser spontaneously coupling to the longitudinal mode structure of the optical cavity and will be discussed in detail later in this paper. Thus, while this method should provide accuracy that can be tied directly to a known frequency standard and a cavity length measurement, the precision of the measurement becomes the largest problem with this technique. We are currently investigating new approaches making use of asymmetric nature of signal resulting from this coupling to improve the precision of the CAPS method.

C. Integrated Cavity Output Spectroscopy

Integrated Cavity Output Spectroscopy (ICOS) makes uses of the steady state power transmitted through the optical system rather than the temporal properties induced by the cavity [2] [10] [11]. Given laser power, P, the differential equation governing the intensity of the light in the cavity is given by

$$\frac{dI}{dt} = \frac{PTc}{2L} - \frac{c\left(1 - R + \alpha\left(\nu\right)\right)}{L} I, \tag{5}$$

where T is the transmission through the mirror. Thus the steady state intensity in the cavity is given by

$$I = \frac{PT}{2\left(1 - R + \alpha\left(\nu\right)\right)} = \frac{PTc}{2L}\tau. \tag{6}$$

Thus, power in the cavity will scale with the decay constant τ. Effectively, this technique allows a steady state absorption method that includes a gain factor because of the effective pathlength due to the optical cavity.

This spectroscopic method has the advantage of using a continuous duty cycle, maximizing the power of the light incident on the detector while completely removing the strenuous demands on the detection electronics to maintain frequency standards or high speed acquisition. The method does, however, share the problem of CAPS spectroscopy because it allows spurious resonant coupling to the longitudinal modes of the optical cavity. ICOS also convolves the time constant with the laser power coupling into the cavity, thereby losing the advantage of CAPS spectroscopy and CRDS where direct measurement of the time constant was possible with an external time or frequency reference. The coupling into the laser cavity is not ideal and behaves somewhat chaotically with a passive optical cavity. Thus, unlike the previous two methods, while precision can be directly quantified, calibration of accuracy requires comparison with a known sample or cross-calibration with another method. Practically, cross-calibration with CRDS and comparison with a known standard should both be implemented in flight.

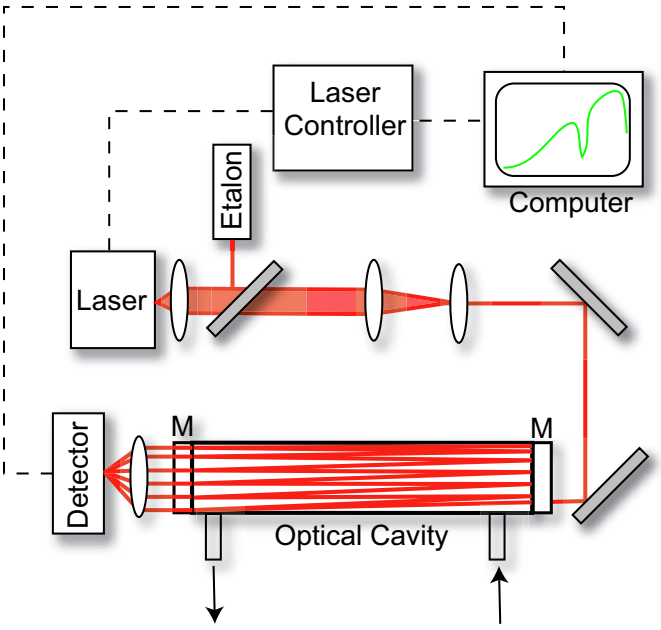

Fig. 1. The design of the instrument requires an optical cavity pumped by a computer controlled laser, monitored by an etalon. The amplified detector output is then reduced and stored on the computer.

In actively locked cavities, spectrometers using this technique have achieved sensitivities of $1.0 \times 10^{-14} cm^{-1}/\sqrt{Hz}$ [12]. Spectrometers with passive cavities using this method have demonstrated sensitivities of $1.0 \times 10^{-10} cm^{-1}/\sqrt{Hz}$, and the limiting factor in those measurements was the spurious coupling to the longitudinal mode structure of the cavity [2].

III. Experimental Design

A. Instrument Layout

All the cavity enhanced spectroscopic techniques share a common instrument layout and capitalize on similar design principles. A schematic layout of the instrument design is shown in Fig. 1. In all cases a narrow-band laser source pumps an optical cavity formed from two highly reflective mirrors. This cavity, into which the sample flows, forms the backbone of the instrument, and the size of the cavity determines the overall size of the instrument. A detector monitors the power escaping from the cavity (which is proportional to the intensity inside the cavity). After subsequent amplification and digitization, a computer is used to reduce, store, and analyze the data.

B. Necessary Design Considerations

Depending on the wavelength region, systems can be constructed with pulsed laser sources, free space coupled laser sources such as Quantum Cascade (QC) lasers, or fiber coupled sources available in the near infrared spectral region [13]. For *in situ* measurements, the fiber coupled lasers are optimal, but in the mid-infrared spectral region, quantum cascade lasers provide the most reliable, high power light sources. However, the QC lasers require liquid nitrogen cooling for high power (40-150 mW), continuous wave operation, making them less

convenient for the airborne environment. In all cases, an etalon is necessary to provide both a power monitor and a calibration source for tuning rate of the laser.

Creating a passive cavity sufficiently robust to maintain alignment under flight conditions requires significant design effort. The cavity design implemented in these experiments rely on three carbon fiber (or Invar) rods with diameter of one inch for stiffness comprising a frame onto which the cell and the optics are mounted. Overall instrument size is primarily determined by the size of the sample cell. Cavity alignment is performed using a kinematic mounting design with fine threaded actuators giving precise angular control (<50 μ rad). Subsequently, we have found that less angular control ($\approx$ 200 μ rad) is sufficient under most circumstances.

Beyond the optical considerations, careful bandwidth matching and qualifying of the detectors, amplifiers, and digitizers is extraordinarily important for cavity enhanced spectroscopy. For any sensitive measurement, narrow bandwidth detectors are advantageous for limiting the electronic noise contributions to the system. However, because the cavity acts as a single pole filter, discerning cavity effects and single pole roll-off in amplification stages can be difficult. In addition, for CRDS in particular, maintaining statistical independence between digitizer samples at a rate far higher than the characteristic frequency of the optical cavity is necessary. Without such statistical independence (i.e. oversampling), quantifying the uncertainty in the fit becomes significantly more difficult because the weight matrix has significant off-diagonal terms. (The weight matrix can be shown to be a tridiagonal matrix for a single pole filter roll off [14].)

Finally, we have found that many simple analysis routines can make assumptions that introduce error into the analysis. We have developed new algorithms for fitting our data to resolve some of these issues, and we have worked to quantify those which we have not resolved.

IV. Technological Improvements

To address the specific initial shortcomings of each method and create the most precise, sensitive, and trustable results possible, we have developed many techniques and approaches to maximize the performance of the cavity enhanced spectrometers while maintaining a flightworthy design.

A. Spurious Coupling to optical resonances

In all stable optical cavities, the cavity has sharp resonances with a free spectral range, FSR, of [15]

$$FSR = \frac{c}{2L}. \tag{7}$$

The light that is transmitted through through the system is necessarily of the character permitted by the etalon. In systems with pulsed light sources, the spectral width of the pulse can be maintained such that it is wide compared to the free spectral range of the cavity thereby ensuring that many longitudinal modes will be excited [1]. Thus, to a pulsed system, the longitudinal modes are relatively unimportant.

For example, with a one meter cavity, the free spectral range is given by 150 MHz. While that FSR is often greater than the transform limit of the pulse, most dye lasers (a very common tunable pulsed source) have limits on the order of 1-5 GHz. Usually, this condition results in the longitudinal mode structure making a negligible contribution to the signal (provided the beating between longitudinal modes is beyond the detection bandwidth).

In systems with continuous wave (cw) light sources, the light sources are typically narrow compared to the FSR of the system, with typical near-infrared diodes having a linewidth on the order of 3 MHz while QC lasers have a linewidth on the order of 1-6 MHz [16]. Thus, with cw systems, coupling to the cavity resonances allows a resonant condition to pass up to 10^4 times more light (for R=99.99%) than the non-resonant condition allows [2]. Of course, only a fraction of that value is ever realized because the system will have a characteristic time of τ before reaching the steady state condition. In practice, without an active lock, the cavity and laser drift in and out of resonance. However, for a 99.99% reflective mirror, maintaining the resonance condition for even $10^{-6}\tau$ will cause 1% noise on the output signal – an unacceptable amount for most measurement strategies. Therefore, to make cw systems usable in flight and to take advantage of the improved duty cycle and more readily available components, we must resolve this issue.

1) Off-axis alignment: In our previous treatment of the free spectral range (yielding (7)), we assumed a stable optical cavity created with two mirrors such that the light met its reentrant condition after 2 cavity lengths. However, if we create a Herriott or Lissajous pattern inside the cavity such that the reentrant condition is met after 2n cavity lengths by introducing the laser off the optical axis of the cavity, we get a new equation for the free spectral range: [17] [18] [19]

$$FSR = \frac{c}{2nL}. \tag{8}$$

For a 200 pass patten, the cavity yields a free spectral range of 1.5 MHz. Because the physical properties of the mirrors remain unchanged, this alignment change must preserve the integrated area under the cavity resonances over a fixed spectral range. By leaving the area invariant (and we can show that the width is constant), we have necessarily reduced the magnitude of the resonances by 100-fold [2]. In theory, this change alone should be sufficient to eliminate the contribution of the coupling to the cavity resonances. In practice, however, we continue to see spurious resonant coupling.

The problem lies with the fact that our model includes only the pattern for the beam centers, but the Gaussian beam profile requires significant separation to avoid interferences in the tails of the beam. In addition, by the same logic, we need to markedly increase the mirror size to accommodate the off-axis alignment pattern without clipping the beam at the end of the mirrors. The stable spot size is determined by the solutions to Maxwell's equations and depends on the wavelength (λ), radius of curvature of the mirrors (r), and cavity length. The

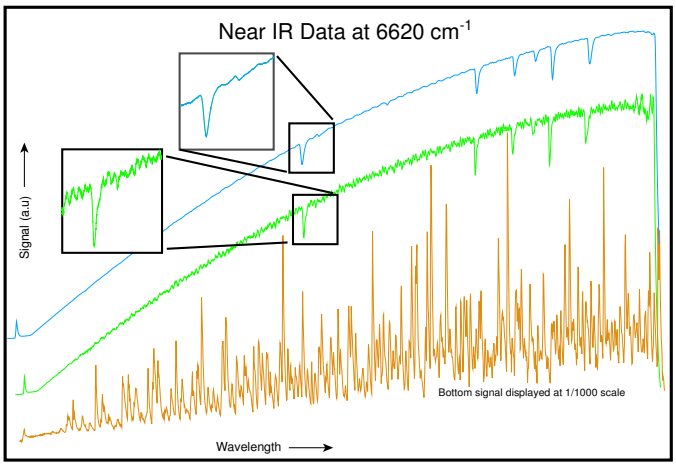

Fig. 2. Off-axis alignment reduces apparent noise due to spurious coupling the longitudinal cavity modes. From top to bottom, the traces show progressively more overlap between adjacent passes through the cavity leading to increased coupling to the longitudinal modes. The lowest trace is shown at 1/1000 scale compared to the upper two traces.

equation for the spot size (s) at the mirrors is given by

$$s = 2\sqrt{\frac{\lambda L}{2\pi}\sqrt{\frac{2r^2}{L\left(r-\frac{L}{2}\right)}}}. \tag{9}$$

Calculating the optimal mirror size require the beams be sufficiently distant from one another and sufficiently distant from the edge of the mirrors. To maintain losses significantly less than the 100 ppm lost per pass due to the mirror itself, the beams should typically be separated from the mirror edge by at least 3-4 beam widths (s).

The result of off-axis alignment can be seen in Figure 2; noise from spurious couplings to the resonances that would otherwise obscure faint spectral lines can be reduced by many orders of magnitude. While significant benefit can be realized by aligning off-axis with reasonably sized mirrors, more work is needed to remove the effect of the spurious resonances. Extremely large mirrors are both costly and create sampling problems because of the large volume of the cell; without reliable sampling, the result can not be trusted regardless of the spectroscopy.

2) Laser line broadening: Another approach to reducing the spurious coupling the the longitudinal cavity modes comes from increasing the laser linewidth. Effectively, this increase will create a situation where the laser line is wide compared to the mode spacing such that the laser will always be putting a fraction of its power into some number of cavity modes, but that fraction will remain constant throughout the scan. This approach is exactly analogous to the favorable situation easily realized with a pulsed laser source.

Many options exist to broaden the laser linewidth, but the three most accessible options are: amplitude modulation, frequency modulation, and changes in the fabrication of the distributed feedback Bragg grating that controls the laser linewidth directly. Amplitude modulation typically produces sidebands on a signal according to the trigonometric identity, [20]

$$\begin{aligned} E(t) &= A\sin\left(\omega_{mod}t\right)\sin\left(\omega_{opt}t\right) \\ &= \frac{A}{2}\left(\cos\left(\omega_{opt}-\omega_{mod}t\right)-\cos\left(\omega_{opt}+\omega_{mod}t\right)\right), \end{aligned} \tag{10}$$

where the electric field is given by $E(t)$, the angular modulating frequency is given by ω_{mod} and the angular optical frequency is given by ω_{opt}. By modulating not with a single frequency, but rather with white noise filtered to have a Gaussian envelope with a maximum at 0 Hertz, we can create a Gaussian laser lineshape of a width wholly determined by the filtering. Commercially available electro-optic modulators operated with custom driving circuitry offer extremely high frequency modulation options and reproduce low frequency components faithfully as well.

The same approach applies with frequency modulation. We can apply Carson's rule to approximate the linewidth, $\Delta\nu$, as a function of the modulation frequency, ω_{mod}, and the modulation depth, ω_{depth}. [20]

$$\Delta\nu \approx 2\left(\omega_{mod}+\omega_{depth}\right) \tag{11}$$

Again, by modulating with white noise with specific amplitude shaped by a filter, we can control the laser linewidth to create an effective linewidth wider than the cavity free spectral range.

3) Dynamic Cavity: Rather than broadening the laser line, the cavity length can also be dithered by $\frac{\lambda}{2}$ using piezoelectric actuators at speeds significantly greater than $f_{3dB}=\frac{1}{2\pi\tau}$ to realize the same effect as broadening the laser linewidth. This dithering motion reduces the time that the cavity will be able to couple to the laser. Significant reductions in the coupling have been observed from f_{3dB} to $4f_{3dB}$; we plan to attempt faster dithering and expect further improvement.

All three of these techniques to reduce the coupling to the longitudinal modes of the cavity may be combined to create a system with a broadened laser entering an off-axis, dynamic cavity. By implementing multiple control strategies, we hope to reduce this contribution to the noise in the data sufficiently to create a passive system that can rival the sensitivities of actively locked systems.

B. Detector Advancements

In recent years, detector technology and amplifier technology have both markedly improved. Multistage thermoelectrically cooled detectors, which do not require liquid nitrogen cooling, are now available to detect wavelength up to $5.5\ \mu m$ with $D^* \approx 10^{12}$. In addition, high gain-bandwidth product ($\geq$1400 MHz) amplifiers with low noise ($\leq 3nV/\sqrt{Hz}$) have been introduced. [21] Coupling these two technologies together, detector/preamplifier combinations can be created that are far superior to those possible previously. For applications like CRDS that require high bandwidths, detector topologies that decouple the shunt resistance of the detector from the stray capacitances in the amplifier have also been investigated. These topologies typically isolate the detector from the

amplifier with a transistor, creating marked improvements in bandwidth without sacrificing the gain in the first amplification stage. This arrangement leads to significantly reduced noise gains, leaving the intrinsic detector noise as the fundamental limit – even at very high signal gain.

C. Fitting Algorithms

When reducing noise throughout the system, the algorithms for data reduction were promptly impugned for both CRDS and ICOS. The data reduction strategies for these apparently simple methods prove very challenging to optimize, and without optimization the noise introduced in the data reduction and analysis easily outweighs the noise from the physical measurement itself.

1) CRDS Exponential Fitting: With Cavity Ringdown Spectroscopy, typical decay constants range from 10μs to 150μs. Thus, 1-8 kHz pulse trains are optimal to allow proper determination of the baseline before and after each exponential transient, while maximizing the duty cycle. Typical data acquisition rates are on the order of 10-50 MHz, so to be feasible in flight, real-time data analysis is advantageous. (Current advancements in storage technology make it no longer necessary, but only barely so.)

A common strategy for data reduction is to average many shots, then attempt to fit them to one exponential [22]. Unfortunately, in any system of this sensitivity, stability is an issue, both of the sample and of the optical system. Coadding many exponentials of the identical time constant, τ, creates no trouble; however, if fluctuations in the cavity or the sample cause fluctuations in the time constant, then coadded signal is actually a complex multiexponential function. There is no reason to believe that the best single exponential functional fit to a multiexponential function will yield a sensible average of the underlying time constants as the exponential is inherently nonlinear.

The correct approach to this problem is to fit each shot individually, find the uncertainty in each fitted time constant and perform a weighted average of those time constants to give the result with the least possible uncertainty. This approach places significant demands on the processing computer or requires post-processing the data. Post-processing, while possible, reduces the ability to adjust duty cycle in flight, to compensate for loss of reflectivity in the mirrors, to diagnose problems in flight, to automatically maintain alignment, etc. Ideally, the fitting should be done in real time.

In order to perform such a fit in real time, only linear fits can be considered; the iterations involved in even the most efficient nonlinear fit algorithms take prohibitively long to perform. However, linearizing exponential functions is significantly more complicated than simply taking the logarithm and taking its derivative into account to modify the weights of the points. By using the derivative, we are asserting that a first order approximation to the noise is appropriate and that the function is not introducing a bias into the system In practice, this assumption is introducing a bias into the system because of the nonlinearity of the logarithmic function. Moreover, in the presence of even very small amounts of noise (signal to noise ratio >100:1), this bias is significant and skews the results compared to a nonlinear fit.

This skew obviously affects the accuracy of the fit, but it also affects the precision because it couples the magnitude of the exponential transient to the value of the fit constant. To first order, these two values should be independent (and physically, they are), but this algorithm couples the two fit coefficients. Because pulsed systems have significant pulse-to-pulse variation, this coupling markedly decreases the precision of the instrument. Even ignoring actual pulse-to-pulse variation within the laser, the coupling into the passive cavity varies slightly creating an even greater discrepancy in the data.

The linear approximation uses the square of the data value multiplied by the original weight ($y^2\sigma_y^2$) for the new weight of each data point. However, empirically, we find much better agreement with the nonlinear fit if we use $y^{0.47}\sigma_y^2$. This adjustment apparently corrects for the nonlinearity of the logarithmic function very efficiently, and yields results that are statistically insignificantly (P>0.1) different from the nonlinear fit.

With the use of the empirical fitting algorithm and by coupling the light into the cavity with a single mode fiber to eliminate pulse-to-pulse mode fluctuations, we can achieve a scanning sensitivity of $2.9\times10^{-11}cm^{-1}/\sqrt{Hz}$ with a passive, flightworthy cavity.

2) ICOS Line Fitting: Similar to CRDS, the data analysis algorithms for ICOS can introduce significant errors into the dataset. Traditional absorption techniques fit the transmission data ($T(\nu)$) to:

$$T(\nu) = \frac{P}{1+\exp\left(-\alpha(\nu)L\right)} \tag{12}$$

The analog to this algorithm for ICOS spectroscopy would be to fit the data to:

$$T(\nu) = \frac{PT^2}{2\left(1-R+\alpha(\nu)L\right)} \tag{13}$$

Both of these equations yield a symmetric lineshape. However, with ICOS spectroscopy, at the optimal scan rate, the lineshape is skewed because the highest frequency components of the signal are attenuated by cavity response. Thus, the proper lineshape is skewed. However, this skewing is not a simple circular convolution because the light of different frequencies is reacting to different losses in the cavity – thus the light interacting with the absorption feature is much less long-lived than the light not interacting with the absorption feature. The proper expression for the light transmitted through the cavity is given by:

$$T(\nu(t)) = \int_0^t \frac{P(t')T^2c}{2L}\exp\left(-\frac{t-t'}{\tau(\nu(t'))}\right)dt' \tag{14}$$

where laser power, P, and wavelength, ν, must both be expressed as functions of time to relate them to the characteristic time of the cavity. Presuming that the laser is scanning in time, this adjustment is valid.

Implementing this algorithm requires a discrete analog to this equation that is beyond the scope of this paper. However, the results from implementing this algorithm markedly improve the internal consistency of the data, both in terms of accuracy and precision.

In addition to implementing the skewed lineshapes, a baseline fitting algorithm for fitting the underlying power curve, $P(t)$, has been developed. Rather than fitting to a polynomial, a singular value decomposition is performed to isolate components of the power spectrum that can be easily removed from the system. The laser sources themselves do not include such periodic events, but the mode structure of the cavity discussed previously does still contribute slightly, and on average, this appears in the data as a very regular, low quality etalon. Effectively, the power curve for the laser physically represents the power of the laser that is coupled into the cavity rather than the actual power from the laser. By properly fitting the baseline and removing periodic components from the etalons created by the cavity, we can reduce the impact of the spurious coupling to the resonant longitudinal modes of the cavity. In Fig. 3, the differences between the two fitting algorithms are readily apparent in the precision and accuracy (as determined from internal consistency only). However, the improvement in the actual fit itself is only apparent upon close inspection of the residual.

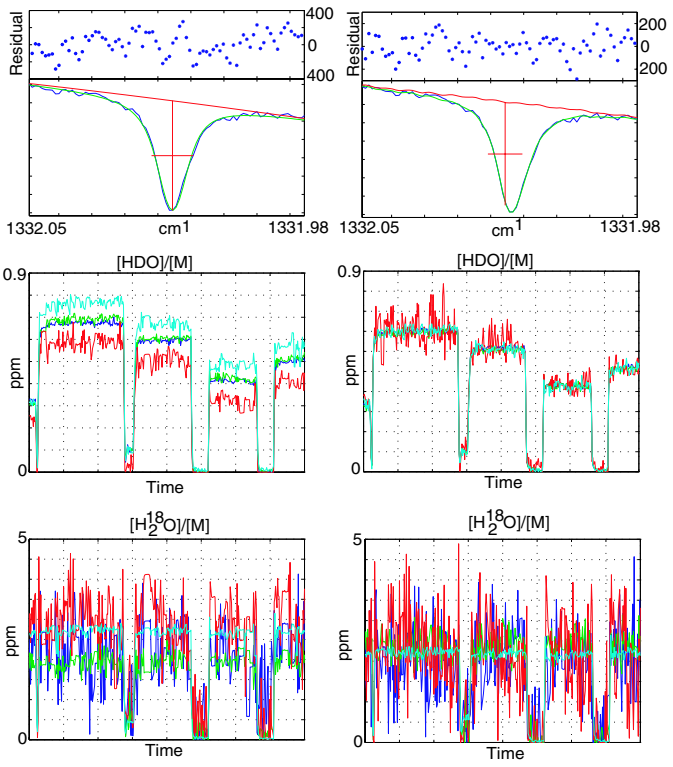

Fig. 3. The advanced fitting algorithm improves internal consistency and precision. The left column shows the traditional fit algorithm, while the right columns shows the algorithm with skew lineshape and singular value decomposition of the baseline. The upper panels show the same line fitted with both methods. The middle panels show HDO lines measured near 1332 cm^{-1}. The concentration as a function of time is plotted as the sample is introduced into and out of the cavity. Agreement between spectral lines of different strengths are much improved with the improved algorithm. The lower panel shows the results of fitting several $H_2^{18}O$ lines in a similar fashion.

V. Conclusion

A. Resultant Instrument Possibilities

Instruments capitalizing on the cavity enhanced spectroscopic techniques, ICOS and CRDS in particular, using passive cavities and flightworthy construction will prove sufficiently robust to withstand the rigors of flight, sufficiently sensitive to make the most demanding measurements, and sufficiently simple to allow easy, trustable calibration and verification. Because all these methods are based on absorption spectroscopy, instruments can be constructed for many different atmospheric species with relative ease. Sampling concerns specific to each species must be addressed, but the detection and analysis will be completely general.

Species such as CO, NO_2, CO_2, N_2O, CH_4, and HCl will be easy targets for this technology, as will any other small molecules and even some larger molecules with advantageous spectroscopic signatures such as RO_2. Also accessible are various isotopomers such as HDO/H_2O, ^{13}CO2/CO2, and ozone isotopomers.

B. Outlook

By creating technology to survey a wide variety of species with simple, reliable methods, we will be able to deliver *in situ* measurements more often, with less time in development, and with more agility than ever before. Such agility will be necessary as the airborne community endeavors to open more collaborations with scientists making satellite observations. Finally, by expanding the suite of available instrumentation for airborne measurements, the community will be able to tailor small, frequent missions to address specific atmospheric questions and to develop specific suites of instruments to link local, regional, and global phenomena through elementary chemical mechanisms and small-scale geophysical events.

Acknowledgment

We would like to credit David S. Sayres, Dr. Jesse Kroll, Dr. Lawrence Lapson, Norton Allen, Joe Demusz, and Mike Greenberg for invaluable contributions to the research efforts in the form of engineering support, advice and scientific support. Without their significant contributions, this work would not have been possible. We are also indebted to the NASA Instrument Incubator Program (IIP) for providing funding for this effort and to Ken Anderson for his support of the research efforts.

References

[1] J. J. Scherer, J. B. Paul, A. O'Keefe, and R. Saykally, "Cavity ringdown laser absorption spectroscopy: history, development, and application to pulsed molecular beams," *Chem. Rev.*, vol. 97, p. 25, 1997.

[2] J. Paul, L. Lapson, and A. J.G., "Ultrasensitive absorption spectroscopy with a high-finesse optical cavity and off-axis alignment," *Appl. Opt.*, vol. 40, p. 4904, 2001.

[3] P. B.A., C. Harb, T. Spence, B. Wilke, J. Xie, J. Harris, and Z. R.N., "Cavity-locked ring-down spectroscopy," *J. App. Phys.*, vol. 83, 1998.

[4] A. O'Keefe and D. A. G. Deacon, "Cavity ringdown optical spectrometer for absorption measurements using pulsed laser sources," *Rev. Sci. Instr.*, vol. 59, p. 2544, 1988.
[5] D. Romanini and K. K. Lehmann, "Ring-down cavity absorption spectroscopy of the very wesk hcn overtone bands with six, seven, and eight stretching quanta," *J. Chem. Phys.*, vol. 99, p. 6287, 1993.
[6] G. Berdenm, R. Peeters, and G. Meijer, "Cavity ring-down spectroscopy: Experimental schemes and applications," *Int. Rev. Phys. Chem*, vol. 19, p. 565, 2000.
[7] K. Lehmann and D. Romanini, "The superposition principle and cavity ring-down spectroscopy," *J. Chem. Phys.*, vol. 105, p. 10263, 1996.
[8] T. G. Spence, C. C. Harb, B. A. Paldus, and R. N. Zare, "A laser-locked cavity ring-down spectrometer employing an analog detection scheme," *Rev. Sci. Instr.*, vol. 71, p. 347, 2000.
[9] J. Herbelin and M. J.A., "Development of laser mirrors of very high reflectivity using the cavity-attenuated phase-shift method," *Appl. Opt.*, vol. 20, p. 3341, 1983.
[10] A. O'Keefe, J. Scherer, and P. J.B., "cw integrated cavity output spectroscopy," *Chem. Phys. Lett.*, vol. 307, p. 343, 1999.
[11] R. Engeln, G. Berdenm, R. Peeters, and G. Meijer, "Cavity enhanced absorption and cavity enhanced magnetic rotation spectroscopy," *Rev. Sci. Instr.*, vol. 69, p. 3763, 1998.
[12] J. Ye, L. Ma, and J. Hall, "Ultrasensitive detections in atomic and molecular physics: demonstration in molecular overtone spectroscopy," *J. Opt. Soc. Am. B*, vol. 15, p. 6, 1998.
[13] J. Faist, F. Capasso, D. Sivco, C. Sirtori, A. Hutchinson, and A. Cho, "Quantum cascade lasers," *Science*, vol. 264, p. 553, 1994.
[14] K. Lehmann, "Conversations of the weight matrices resulting from exponential covariance matrices," May 1999.
[15] A. Yariv, *Introduction to Optical Electronics*, 2nd ed. New York, NY: Holt, Rinehart and Winston, 1976.
[16] D. Weidmann, L. Joly, V. Parpillon, D. Courtois, Y. Bonetti, T. Aellen, M. Beck, J. Faist, and D. Hofstetter, "Free-running 9.1-mu m distributed-feedback quantum cascade laser linewidth measurement by heterodyning with a (co2)-o-18 laser," *Opt. Lett.*, vol. 28, p. 704, 2003.
[17] D. Herriott, R. Kompfner, and H. Kogelnik, "Off-axis paths in spherical mirror interferometers," *Appl. Opt.*, vol. 3, p. 523, 1964.
[18] D. Herriott and H. Schulte, "Folded optical delay lines," *Appl. Opt.*, vol. 4, p. 883, 1965.
[19] J. McManus, P. Kebabian, and W. Zahniser, "Astigmatic mirror multipass absorption cells for long-path-length spectroscopy," *Appl. Opt.*, vol. 38, p. 3336, 1995.
[20] F. Strembler, *Introduction to Communications Systems*, 3rd ed. Boston, MA: Addison-Wesley, 1990.
[21] "Texas Instruments, Inc." [Online]. Available: http://www.ti.com
[22] R. van Zee, J. Hodges, and J. Looney, "Pulsed, single-mode cavity ringdown spectroscopy," *Appl. Opt.*, vol. 38, p. 3951, 1999.